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(54) FINE PARTICLE FOR MODIFYING POLYOLEFIN

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain fine particles having a good affinity with a polyolefin and a high clarity by forming fine particles each comprising a core of which the difference in refractive index from a polyolefin is a specified value or lower and a shell layer which is formed on the surface of the core and has a solubility parameter different from that of a polyolefin by a specified value or lower.

SOLUTION: Each of the fine particles comprises a core of which the difference in refractive index from a polyolefin is 0.05 or lower and a shell layer which is formed on the surface of the core and has a solubility parameter different from that of a polyolefin by 3.0 MPa^{1/2} or lower. An inorg. material (e.g. silica or titanium oxide) or an org. polymer (e.g. an acrylic resin) is used as the core. The shell layer is formed from a polymer of a styrene monomer or an olefin monomer and is pref. crosslinked or grafted onto the core. The product of the shell layer thickness and the difference in refractive index from a polyolefin is required to be 20 nm or lower for obtaining clarity. 100 pts.wt. polyolefin is mixed with 0.01-50 pts.wt. fine particles above-described and then is formed into a film, etc.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the particle for polyolefine reforming. Furthermore, it is related with the particle which reforms a polyolefine, without excelling in compatibility with a polyolefine and spoiling the transparency of this polyolefine in detail.

[0002]

[Description of the Prior Art] Conventionally, the method of reforming the property of a polyolefine is learned by adding a particle to a polyolefine. As a method especially of preventing blocking of films with a polyolefine film, the method of adding macromolecule bridge formation particles, such as non-subtlety particles and polystyrene, such as a silica and titanium oxide, and a polymethylmethacrylate, is used widely.

[0003] For example, after carrying out the amount mixture of specification and carrying out melting extrusion of the macromolecule pulverized coal which has the structure of cross linkage with a particle size of 3-40 micrometers, and does not have the melting point to a polypropylene resin, it cools to JP,57-64522,A and the extension polypropylene system film which extended this to at least 1 shaft orientations, and was obtained is indicated. Moreover, when the difference of the solubility coefficient of the crosslinked polymer of non-** and a polypropylene resin is small in this official report, the transparency of the film with which the adhesion of a crosslinked polymer and a polypropylene resin was extended well is good, the bird clapper is indicated, and the pulverized coal of the crosslinked polymer which makes basic structure polyethylene, polypropylene, polystyrene, a polymethylmethacrylate, a polycarbonate, a polyethylene terephthalate, etc. as an example is mentioned.

[0004] The polyolefine film which becomes JP,6-107868,A from the constituent which blended with the polyolefine the bridge formation particle which is 0.4-7 micrometers of mean particle diameters by the copolymer which makes an acrylic monomer and a styrene system monomer a principal component is indicated.

[0005] Moreover, the polyolefine film with which all or some of particle front face of a crosslinked-polymer particle (A) obtained by carrying out the polymerization of the polymerization nature monomer which contains 10% of the weight or more of a cross-linking monomer in JP,7-228729,A as a core-shell-like modifier blended the composite-ized crosslinked-polymer particle of 0.01-10 micrometers of mean particle diameters which it comes to cover with thermoplastics (B) is indicated.

[0006]

[Problem(s) to be Solved by the Invention] However, by the particle for polyolefine reforming of these former, it was difficult to obtain what has the property of both the transparency of a polyolefine, and the compatibility between a polyolefine and a particle.

[0007] For example, since particles, such as a silica and a bridge formation polymethylmethacrylate, have a refractive index close to a polyolefine, although transparency is good, since compatibility with a polyolefine is inadequate, when the fabricating operation of the polyolefine is carried out, exfoliation with a particle and a polyolefine tends to take place, and problems, such as generating of a void and omission of a particle, arise.

[0008] On the other hand, although it excels in compatibility with a polyolefine and neither a void nor the problem of omission can arise easily by the bridge formation polystyrene system particle, since the refractive index with a polyolefine is not in agreement, the transparency of a polyolefine gets worse.

[0009] Moreover, although the property of both compatibility and transparency can be made to balance when the copolymer particle which consists of a styrene system monomer and an acrylic (meta) monomer is used, a polymethylmethacrylate system particle is not attained to in respect of transparency, but it is less than a polystyrene system particle also to a void or omission.

[0010] Furthermore, problems [when many acrylic monomers are used for a shell layer as shown in the example of JP,7-22879,A even if it used the compound polymer particle which consists of a high core layer of crosslinking density and a low shell layer of crosslinking density, compatibility with a polyolefine is not necessarily enough, and], such as a void at the time of extension fabrication or omission, were not completely solvable.

[0011] It is in the purpose of this invention offering the particle for polyolefine reforming which reforms a polyolefine, without excelling in compatibility with a polyolefine and spoiling the transparency of a polyolefine.

[0012]

[Means for Solving the Problem] That is, this invention is a particle for polyolefine reforming characterized by having the shell layer whose solubility-parameter differences with this polyolefine are 1/2 or less 3.0MPa(s) at the core layer whose refractive-index difference with this polyolefine it is a particle for polyolefine reforming and is 0.05 or less, and the surface of this core layer.

[0013]

[Embodiments of the Invention] As for the particle for polyolefine reforming of this invention, a refractive-index difference with this polyolefine has 0.03 or less core layer preferably 0.05 or less. When the refractive-index difference of a core layer and a polyolefine became larger than 0.05 and the particle for reforming of this invention is added and used for a polyolefine, it is not desirable in order to spoil the transparency of a polyolefine.

[0014] As a core layer, organic macromolecules, such as non-element material, such as a silica and titanium oxide, acrylic resin, polystyrene, polyester, a polyolefine, and silicone resin, etc. can be used.

[0015] Furthermore, the particle for polyolefine reforming of this invention has the shell layer whose solubility-parameter differences with this polyolefine are 1/2 or less 3.0MPa(s) on the front face of the aforementioned core layer. If the solubility-parameter difference of a shell layer and a polyolefine becomes larger than one half 3.0 MPas, in case the compatibility of the particle for reforming of this invention and a polyolefine will be inferior and the fabricating operation of this polyolefine will be carried out, the problem of generating and defluxion of a void is started, and it becomes impossible to discover still more sufficient reforming effect. It is connected with the void and dirt of mold goods as a result, and the dirt of the roll by omission of a particle has desirable how to twist, although the very thing will be allowed if a few [the very thing]. On the other hand, since a void is the blemish of the mold goods itself, its how to twist is desirable.

[0016] For the solubility parameter of this invention, it defines as a 3-dimensional parameter [having been advocated by Hansen and C.M. (deltad, deltap, deltah)], and difference deltadelta of a solubility parameter is the following formula. It is defined like a-one number by the distance for two points within a 3-dimensional coordinate.

[0017]

[Equation 1] The solubility parameter of $\text{deltadelta}^2 = (\text{deltad1} - \text{deltad2})^2 + (\text{deltap1} - \text{deltap2})^2 + (\text{deltah1} - \text{deltah2})^2$ each matter is shown in "Handbook of Solubility Parameters and Other Cohesionparameters (2nd Ed.) etc." (CRC publication). Moreover, how to compute from group mol nominal tractive capacity is also shown.

[0018] Although it can concern and use for inorganic and organic as a shell layer, it is desirable to use an organic system macromolecule. Furthermore, it is more desirable to use the macromolecule which mainly consists of a styrene system monomeric unit or an olefin system monomeric unit. When using an organic system macromolecule as a shell layer, as for a shell layer, it is desirable to carry out a graft to

bridge formation or a core layer. Bridge formation or when the graft was carried out, it adds to a polyolefine and melting kneading is carried out, a shell layer separates from a core layer and hardly diffuses a shell layer in a polyolefine, and compatibility can be effectively improved between the particle for reforming, and a polyolefine.

[0019] Moreover, as for the particle for polyolefine reforming of this invention, it is desirable that a product ($\Delta n \cdot d$) with the refractive-index difference (Δn) of the thickness (d) of the shell layer, a shell layer, and polyolefin resin sets 20nm or less to 10nm or less preferably. If $\Delta n \cdot d$ becomes larger than 20nm, that is, a shell layer becomes thick or a refractive-index difference with a polyolefine becomes large, since light will be greatly scattered about by the amount of shell layer, the transparency of a polyolefine falls.

[0020] When the mean particle diameter of a core layer is known in this invention, this value, the value calculated from the mean particle diameter of a core-shell particle, and the value calculated from the volume ratio and mean particle diameter of the used core layer and a shell layer are used for the thickness of a shell layer. For example, since the used monomer becomes whole-quantity polymer mostly, in the case of the resin obtained by carrying out 2 stage polymerization of a core layer and the shell layer, it asks for the volume ratio of polymer, and it is asked from the mean particle diameter of this value and a core-shell particle.

[0021] The method of mixing the particle which serves as a shell layer at the particle used as a core layer as a method of obtaining the particle of the shape of a core shell like this invention with dry type or wet, and obtaining a composite particle, the method of carrying out the polymerization of a core layer and the shell layer in two stages by the emulsion-polymerization method or the distributed polymerization method, etc. are learned. As a method which is mixed with dry type or wet and composite-izes a particle The coating method using the fluid bed (the 26 - 30 pages of for example, the "chemical engineering" March, 1996 issues), The mechanofusion method using the sheared type mill (the 34 - 42 pages of for example, the "chemical engineering" September, 1995 issues), The hybridization method using the striking energy in a high-speed flow There are (for example, "Society of Powder Technology, Japan" 33 volume 8 No. 35-43 page (1996)), a hetero condensation method (for example, "chemical engineering collected-works" 18 volume 5 No. 637-642 page (1992)) which mixes an amphoteric latex. Moreover, the method of obtaining a core-shell-like particle using two steps of the emulsion-polymerization methods or a distributed polymerization method is also learned widely (for example, J.of Polym.Sci.Polym.Chem.Ed. 16, 3219, etc. (1980)). In order to carry out the graft of the shell to bridge formation or a core layer, the core-shell-like particle production method by the latter polymerization is suitable.

[0022] The particle of this invention is added and used for a polyolefine. With a polyolefine, the copolymers of a homopolymer or a copolymer, these alpha olefins and the monomers which can be copolymerized (for example, vinyl acetate, a maleic acid, etc.), and an alpha olefin and such polymer mixture of alpha olefins, such as a propylene, ethylene, 1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene, are mentioned.

[0023] According to a use, although the amount which the particle for polyolefine reforming uses is various, it usually carries out 0.01-50 weight section use to the polyolefine 100 weight section. The method which does not receive limitation if it is the method which a particle distributes uniformly as a method of adding a particle to a polyolefine, is mixed by the ribbon blender, the Henschel mixer, etc., for example, carries out melting mixture of the mixture with an extruder is suitable. In addition, a well-known antioxidant, a neutralizer, lubricant, a non-drop agent, an antistatic agent, etc. can be suitably blended if needed at this time. The polyolefine by which the particle was added is fabricated by the well-known method by the film, and is used. Especially, it is suitable for the film extended by at least 1 shaft orientations.

[0024]

[Effect of the Invention] The particle for polyolefine reforming of this invention is excellent in the transparency of a polyolefine, and concordance with a polyolefine, has generating of a void, and dropping out [little], when extension processing etc. is performed to the polyolefine which added

especially this particle, and can fully demonstrate a reforming function.

[0025]

[Example] this invention is not limited by these although an example explains this invention concretely.

[0026] In addition, since the influence of the compatibility of a polyolefine and the particle for reforming appears notably, the example in the biaxial oriented film of polypropylene is shown. The result of evaluation of each example and the example of comparison is shown in Table 2.

[0027] Fabrication of a biaxial oriented film is performing a melting knockout at the resin temperature of 260 degrees C, and quenching the mixture of the polypropylene 100 weight section and the particle 0.4 weight section for reforming in a 60-degree C cooling roller. 0. The corona treatment was given to one side after carried out [at the shape of a sheet of 8 mm] cooling solidification and extending 5 times to lengthwise at the extension temperature of 145 degrees C continuously according to the roll peripheral-speed difference of an after [a preheating] and length drawing machine, extending 8 times in a longitudinal direction at the extension temperature of 157 degrees C in a tenter formula drawing machine succeedingly, heat-treating at 165 degrees C and considering as an oriented film with a thickness of 20 micrometers. Film production was continued for 2 hours and the grade of the dirt by the particle for reforming of the above-mentioned vertical extension roll was judged by viewing.

[0028] The Hayes measurement of a film is ASTM. It measured based on D-103.

[0029] From mol nominal tractive capacity, the solubility parameter of the various macromolecules used for the polypropylene and the particle for reforming which were used in the example computed the Hansen parameter, and searched for the solubility difference with polypropylene. A calculation result is shown in Table 3.

[0030] The thickness of a shell layer was calculated by calculation from the volume ratio of a core layer / shell layer from the used amount of monomers, and was calculated from the mean particle diameter. The calculation result was shown in Table 1.

[0031] The methanol 40 weight section, the styrene 4 weight section, the 2-ethylhexyl acrylate 6 weight section, the 55% divinylbenzene 1 weight section, the hydroxypropylcellulose 0.05 weight section, and the t-butylperoxy-2-ethylhexanoate 0.2 weight section were taught to the airtight container with example 1 (production of particle) agitator, the polymerization was carried out at 90 degrees C after the dissolution for 10 hours, and the refractive index 1.51 and the particle of 1.3 micrometers of mean particle diameters were obtained. Subsequently, it was left at 60 more degrees C after addition for 4 hours, having applied the mixed solution of the methanol 12 weight section, styrene 3 weight section, 55% divinylbenzene 0.2 weight section, 2, and 2'-azobis (2,4-dimethylvaleronitrile) 0.06 weight section for 40 minutes at 60 degrees C, the polymerization was completed, and the particle whose mean particle diameter is 1.4 micrometers was obtained. The thickness of the shell layer for which it asked from the core / shell volume ratio of the obtained particle was about 60nm. The property of a particle is shown in Table 1.

(Evaluation with a biaxial extension polypropylene film) As the particle 0.4 weight section obtained by the polypropylene (refractive-index 1.51 and melt index 2.5g / 10 minutes) 100 weight section and a stabilizer. The stearic-acid-ester 2 weight section of a stearyl diethanolamine was mixed as the calcium-stearate 0.1 weight section, 2, the 6-t-butylhydroxytoluene 0.2 weight section, the antioxidant (Irganox1010:Ciba-Geigy) 0.05 weight section, and an antistatic agent, and biaxial oriented-film fabrication was performed by the method described previously using this mixture. Most dirt of the roll by the particle cannot be found and the film also with good transparency was obtained.

[0032] The particle was produced like the example 1 except having made into the mixed solution of the methanol 20 weight section, styrene 5 weight section, 55% divinylbenzene 0.4 weight section, 2, and 2'-azobis (2,4-dimethylvaleronitrile) 0.1 weight section the monomer solution dropped at the 22nd step of example. The thickness of 1.5 micrometers of mean particle diameters and a shell layer was about 100nm. Biaxial oriented-film fabrication was performed like the example 1 using the obtained particle. Most dirt of the roll by the particle cannot be found and the film also with good transparency was obtained.

[0033] The particle was produced like the example 1 except having made into the mixed solution of the

methanol 40 weight section, styrene 10 weight section, 55% divinylbenzene 0.8 weight section, 2, and 2'-azobis (2,4-dimethylvaleronitrile) 0.2 weight section the monomer solution dropped at the 32nd step of example. The thickness of 1.6 micrometers of mean particle diameters and a shell layer was about 170nm. Biaxial oriented-film fabrication was performed like the example 1 using the obtained particle. Most roll dirt by the particle was usable, although there is nothing and the transparency of a film fell for a while.

[0034] Biaxial oriented-film fabrication was performed using the particle of only a core layer without adding the 2nd step of monomer solution by the particle production method of example of comparison 1 example 1. Although the good film of transparency was obtained, the roll dirt by the particle was intense and the lump of a particle which separated and fell from the roll was imprinted also on the film.

[0035] The methanol 40 weight section, the styrene 10 weight section, the 55% divinylbenzene 1 weight section, the hydroxypropylcellulose 0.05 weight section, and the t-butylperoxy2-ethylhexanoate 0.2 weight section were taught to the airtight container with example of comparison 2 agitator, the polymerization was carried out at 90 degrees C after the dissolution for 10 hours, and the refractive index 1.59 and the particle of 1.3 micrometers of mean particle diameters were obtained. Biaxial oriented-film fabrication was performed for the obtained particle like the example 1. The transparency of a film was low although most dirt of the roll by the particle could not be found.

[0036] Biaxial oriented-film fabrication was performed like the example 1 using the PMMA particle (total MR2 made from ***** G, 2 micrometers of mean particle diameters, a refractive index 1.49) of example of comparison 3 marketing. The roll dirt by the particle was intense and it was observed that many voids have occurred in a film.

[0037] The methanol 40 weight section, the styrene 7.5 weight section, the methyl methacrylate 2.5 weight section, the 55% divinylbenzene 1 weight section, the hydroxypropylcellulose 0.05 weight section, and the t-butylperoxy2-ethylhexanoate 0.2 weight section were taught to the airtight container with example of comparison 4 agitator, the polymerization was carried out at 90 degrees C after the dissolution for 10 hours, and the refractive index 1.57 and the particle of 1.6 micrometers of mean particle diameters were obtained. Biaxial oriented-film fabrication was performed for the obtained particle like the example 1. Although there was almost no roll dirt by the particle, it was observed that the void has occurred in a film.

[0038]

[Table 1]

	添加微粒子						
	コア層		シェル層				粒径 μm
	組成	屈折率	組成	$\Delta\delta$	屈折率	厚み $\Delta n \times d$	
実施例 1	ST/2EHA 架橋モノマー	1.51	ST 架橋 重合体	2.1	1.59	60nm 4.8nm	1.4
実施例 2	"	"	"	"	"	100nm 8.0nm	1.5
実施例 3	"	"	"	"	"	170nm 14nm	1.6
比較例 1	"	"	なし コア $\Delta\delta=3.9$				1.3
比較例 2	ST 架橋モノマー	1.59	なし コア $\Delta\delta=2.1$				1.3
比較例 3	MMA 架橋モノマー	1.49	なし コア $\Delta\delta=8.6$				2.0
比較例 4	ST/MMA 架橋モノマー	1.57	なし コア $\Delta\delta=2.8$				1.6

ST: Styrene, 2EHA:2-ethylhexyl acrylate, a solubility-parameter difference with MMA:methyl methacrylate $\Delta\delta$:polypropylene (unit : MPa^{1/2})

[0039]

[Table 2]

	フィルム構成		評 価			
	ポリプロピレン 重量部	微粒子 重量部	ロール汚れ	ヘイズ %		欠陥 観察
				トータル	内部	
実施例1	100	0.4	△	3.3	0.9	○
実施例2	"	"	○	3.3	0.9	○
実施例3	"	"	○	4.7	2.2	○
比較例1	"	"	×	3.3	0.7	△
比較例2	"	"	○	5.8	2.8	○
比較例3	"	"	×	2.2	1.0	×
比較例4	"	"	○	3.9	1.5	△

roll dirt and void evaluation O: -- almost -- nothing and **: -- a few -- it is -- x: -- it is -- those with
xx:remarkable [0040]

[Table 3]

	Hansen溶解度 パラメータ (MPa ^{1/2})			ポリプロピレン との溶解度 パラメータ差 (MPa ^{1/2})
	δ_d	δ_p	δ_h	
ポリプロピレン	17.1	0	0	0
ポリメチルメタクリレート	17.9	3.4	7.9	8.6
ポリスチレン	19.2	0.6	0	2.1
ポリ2-エチルヘキシルアクリレート	17.9	2.0	5.5	5.8
スチレン/2-エチルヘキシルアクリレート共重合体 (6/4)	18.3	1.5	3.5	3.9
スチレン/メチルメタクリレート共重合体 (3/1)	18.9	1.3	1.7	2.8

[Translation done.]